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THERMAL DIFFUSION OF BINARY GASEOUS MIXTURES

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ABSTRACT. Rigorous theoretical formulae according to Chapman and Cowling, and Kihara approximation schemes have been derived for the thermal diffusion factor of such binary mixtures where the lighter component is in trace, from the known expressions for the general case. These formulae are further simplified by expanding in powers of the ratio of molecular masses. The latter expressions are simpler and preferable for numerical computation. Sample numerical calculations reveal that the convergence of the theoretical formulae for this case is poorer as compared to the other end of the composition range, the magnitude depends upon the system and the temperature range.

INTRODUCTION

Recent attempts, Weissman, Saxena and Mason (1961), Saxena and Mason (1959), Heymann and Kistemaker (1959), Mundy (1958), Grew, Johnson and Neal (1954), and Grew and Ibbs (1952), to measure accurately the thermal diffusion factor, α_T, have necessitated an accurate knowledge of the theoretical expression for α_T, so that a precise interpretation of the experimental data may be possible. A considerable achievement is due to Mason (1957), who extended the formulae to higher approximations and performed calculations for some ideal mixtures. Real systems differ from these ideal mixtures and the conclusions derived from the latter may not hold for the former, at least quantitatively. For this reason, Saxena and Dave (1961) investigated the binary mixtures where the heavier component was in trace. In this paper those binary mixtures are considered which have the lighter component in trace, and therefore provide the other end of the composition range. These two investigations together besides enabling to estimate the entire composition dependence of α_T also facilitate analysis of experimental data of binary systems where one component is a radioactive gas and is in trace. A knowledge of the appropriateness of these approximation schemes at the two limiting ends may also provide some clue for the use of these schemes in assessing α_T expression for the middle range of the composition. Theoretical expressions of α_T derived according to the approximation procedures of Chapman and Cowling (1952) and Kihara (1949, 1953) have been considered. The rigorous expressions are further simplified by expanding in powers of M, where $M = (M_2/M_1)$ and M_2 and M_1 are the molecular weights of the lighter and heavier components respectively. Convergence errors as well as the adequacies

of the simpler expressions are investigated by performing calculations for the specific systems. Some preliminary results have been reported by us (1962) earlier.

FORMULAE FOR α_T

Chapman and Cowling Method

The general m-th approximation to α_T is given by Chapman and Cowling (1952). To the first approximation for binary systems when the lighter component is in trace we get

$$[\alpha_T]_1 = \frac{5}{2}\left[\left(\frac{M_1+M_2}{2M_1}\right)^{\frac{1}{2}}\left(\frac{a_{10}a'_{-1-1}-a_{10}a_{-11}}{a''_{11}a'_{-1-1}}\right)\right.$$

$$\left.+\frac{a_{-10}}{a'_{-1\ 1}}\left(\frac{M_1+M_2}{2M_2}\right)^{\frac{1}{2}}\right]. \qquad \ldots (1)$$

The various a_{ij} are functions of molecular weights of the two gases, and collision integrals, and are given by Mason (1954, 1957). Equation (1) can be put in the more familiar form as follows :

$$[\alpha_T]_1 = (6C_{12}^*-5)(S_1/Q_1), \qquad \ldots (2)$$

where

$$S_1 = \frac{M_1}{M_2}\left(\frac{2M_2}{M_1+M_2}\right)^{\frac{1}{2}}Z' - \frac{4M_1M_2A^*_{12}}{(M_1+M_2)^2} - \frac{15M_2(M_2-M_1)}{2(M_1+M_2)^2}, \qquad \ldots (3)$$

$$Q_1 = \frac{2Z'}{M_2(M_1+M_2)}\left(\frac{2M_2}{M_1+M_2}\right)^{\frac{1}{2}}\left[\left(\frac{5}{2}-\frac{6}{5}B_{12}^*\right)M^2_1\right.$$

$$\left.+3M^2_2+\frac{8}{5}M_1M_2A^*_{12}\right], \qquad \ldots (4)$$

$$A_{12}^* = \frac{\Omega_{12}^{(2,2)*}}{\Omega_{12}^{(1,1)*}}, \quad B^*_{12} = \frac{5\Omega_{12}^{(1,2)*}-4\Omega_{12}^{(1,3)*}}{\Omega_{12}^{(1,1)*}},$$

$$C_{12}^* = \frac{\Omega_{12}^{(1,2)*}}{\Omega_{12}^{(1,1)*}} \quad \text{and} \quad Z' = \frac{\Omega_{11}^{(2,2)*}\sigma_{11}^2}{\Omega_{12}^{(1,1)*}\sigma_{12}^2} \qquad \ldots (5)$$

Here $\Omega_{ij}^{(l,m)*}$ are dimensionless reduced collision integrals and are defined so as to be equal to unity for rigid spherical molecules of mutual diameter σ_{ij}, Hirschfelder,

Curtiss and Bird (1954). For such mixtures, the second approximation to α_T is given by

$$[\alpha_T]_2 = \frac{5}{2}\left[\left(\frac{M_1+M_2}{2M_1}\right)^{\frac{1}{2}}\{(a'_{-1-1}a'_{-2-2}-a'^2_{-1\ 2})(a''_{11}a''_{22}-a''^2_{12})\}^{-1}\right.$$

$$\{(a_{10}a''_{22}-a''_{12}a_{02})(a'_{-1-1}a'_{-2-2}-a'^2_{-1-2})$$

$$+(a_{1-1}a''_{22}-a''_{12}a_{2-1})(a_{20}a'_{-1\ 2}-a_{-10}a'_{-2\ 2})$$

$$+(a_{1-2}a''_{22}-a''_{12}a_{2-2})(a_{-10}a'_{-1-2}-a_{-20}a'_{-1-1})\}$$

$$\left.+\left(\frac{M_1+M_2}{2M_2}\right)^{\frac{1}{2}}\left(\frac{a_{-10}}{a'_{-1-1}}\right)\left(1-\frac{a_{-20}a'_{-1\ 2}}{a_{-10}a'_{-2-2}}\right)\left(1-\frac{a'^2_{-1-2}}{a'_{-1-1}a'_{-2\ 2}}\right)^{-1}\right]. \quad \cdots \quad (6)$$

Considerable simplification occurs in the expressions of α_T if they are expanded in terms of the ratio (M_2/M_1). Thus, for the first approximation we get

$$[\alpha_T]_1 = \frac{(6C_{12}^*-5)}{2Y}\left[1-\left(\frac{8A_{12}^*}{5Y}-1\right)M+\frac{15}{2\sqrt{2}Z'}\left(1-\frac{8}{15}A_{12}^*\right)M^{3/2}\right.$$

$$\left.-\frac{3}{Y}\left\{1-\frac{8}{15}A_{12}^*\left(\frac{8A_{12}^*}{5Y}-1\right)\right\}M^2+\ldots\right], \quad (7)$$

where

$$Y = (1/10)(25-12B_{12}^*). \quad (8)$$

Similarly, for the second approximation we get

$$[\alpha_T]_2 = [\alpha_T]_1^a(1+B_1M+B_2M^2)[(1-B_{14})^{-1}$$

$$\{1-B_{14}(B_3+B_5)(1-B_{14})^{-1}M+B_{14}(1-B_{14})^{-1}$$

$$(B_{14}(B_3+B_5)^2(1-B_{14})^{-1}+B_4+B_6+B_3B_5)M^2\}]$$

$$[1-(1+B_5M+B_6M^2)(B_9B_{13}/B_{10})]-\frac{5\sqrt{2}}{16Z'}$$

$$(6C_{12}^*-5)(1-B)^{-1}(5B_{10}Y-4B_9^2)^{-1}[10YB_{10}-BB_9^2$$

$$-B_{11}(B_{10}-B_9B_{13})-B_{12}(10YB_{13}-8B_9)]M^{3/2}$$

$$+\quad\cdots \quad (9)$$

where

$$[\alpha_T]_1^a = (6C_{12}^*-5)/2Y,$$

$$B = (8E_{11}^*-7)^2(77-112E_{11}^*+80F_{11}^*)^{-1},$$

$$B_1 = 1-(8A_{12}^*/5Y),$$

$$B_2 = (8A_{12}^*/5Y)^2 + (15 + 8A_{12}^*)(5Y)^{-1},$$

$$B_3 = (7A_{12}^* - 8H_{12}^*)(B_9)^{-1} + (8A_{12}^*/5Y),$$

$$B_4 = \frac{21(5 - 6C_{12}^*)}{8B_9} + \frac{3}{Y} - \frac{8A_{12}^*(7A_{12}^* - 8H_{12}^*)}{5YB_9},$$

$$B_5 = (7A_{12}^* - 8H_{12}^*)B_9^{-1} - B_7B_{10}^{-1} + \frac{64A_{12}^{*2}}{25Y^2},$$

$$B_6 = \frac{21(5 - 6C_{12}^*)}{8B_9} + \frac{B_7(7A_{12}^* - 8H_{12}^*)}{B_9B_{10}} + \frac{B_7^2}{B_{10}^2} - \frac{B_8}{B_{10}},$$

$$B_7 = (49/2)A_{12}^* - 56H_{12}^* + 40F_{12}^*A_{12}^*,$$

$$B_8 = (735/16) + 12K_{12}^* - 90C_{12}^* - (81/4)B_{12}^*,$$

$$B_9 = (175/32) + (225/16)C_{12}^* - 15G_{12}^* - (57/8)B_{12}^*,$$

$$B_{10} = (1225/128) + (315/4)C_{12}^* - (399/16)B_{12}^* + 45J_{12}^* - 105G_{12}^*,$$

$$B_{11} = 55 - 12B_{12}^* - 16A_{12}^*,$$

$$B_{12} = (595/32) + (3/16)C_{12}^* - (57/8)B_{12}^* - 15G_{12}^* - 7A_{12}^* + 8H_{12}^*,$$

$$B_{13} = \left[1 - \frac{3(5 - 4B_{12}^*)}{4(6C_{12}^* - 5)}\right]$$

$$B_{14} = 4B_9^2/5B_{10}Y,$$

and

$$E_{ij}^* = \frac{\Omega_{ij}^{(2,3)*}}{\Omega_{ij}^{(2,2)*}}, \quad F_{ij}^* = \frac{\Omega_{ij}^{(2,4)*}}{\Omega_{ij}^{(2,2)*}}$$

$$G_{ij} = \frac{\Omega_{ij}^{(1,4)*}}{\Omega_{ij}^{(1,1)*}}, \quad H_{ij}^* = \frac{\Omega_{ij}^{(2,3)*}}{\Omega_{ij}^{(1,1)*}},$$

$$J_{ij}^* = \frac{\Omega_{ij}^{(1,5)*}}{\Omega_{ij}^{(1,1)*}}, \quad K_{ij}^* = \frac{\Omega_{ij}^{(3,3)*}}{\Omega_{ij}^{(1,1)*}}. \qquad \ldots (10)$$

If we put $M = 0$ in Eqs (7) and (9), α_T expressions corresponding to Lorentzian gas mixtures result. These are

$$[\alpha_T]_1 = [\alpha_T]_1^a,$$

$$[\alpha_T]_2 = [\alpha_T]_1^a[1 - (B_9B_{13}/B_{10})][1 + (4B_9^2/5YB_{10})]^{-1}.$$

These expressions were earlier derived by Mason (1957).

Kihara and Extended Kihara Methods

To the first approximation when the lighter component is in trace the thermal

diffusion factor, $[\alpha'_T]_1$, is again given by an expression similar to Eq. (2), except Q_1 which is now defined as follows.

$$Q'_1 = \frac{2Z'}{M_2(M_1+M_2)}\left(\frac{2M_2}{M_1+M_2}\right)^{\frac{1}{2}}\left[M_1^2+3M_2^2+\frac{8}{5}M_1M_2A_{12}^*\right] \quad \ldots \quad (11)$$

The second approximation to α_T for such mixtures is

$$[\alpha'_T]_2 = [\alpha_T]_1(1+K'_1)+K'_2,$$

where

$$K'_1 = \frac{C''^2_{-1-1}}{C''_{-1-1}C''_{-2-2}} - 1 + \frac{C''^2_{12}}{C''_{11}C''_{22}}, \quad (12)$$

and

$$K'_2 = \frac{5}{2}\left(\frac{M_1+M_2}{2M_1}\right)^{\frac{1}{2}}\left[\frac{a_{-10}C'_{1-2}C''_{-1-2}}{C''_{11}C''_{-1-1}C''_{-2-2}} - \frac{a_{10}C''^2_{-1-2}}{C''_{11}C''_{-1-1}C''_{-2-2}}\right.$$

$$+\frac{C'_{-12}a_{0-1}C''_{12}}{C''_{22}C''_{-1-1}C''_{11}} \quad \frac{C_{2-2}C''_{-1-2}a_{0-1}C''_{12}}{C''_{22}C''_{-2-2}C''_{-1-1}C''_{11}} - \frac{a_{0-2}C'_{1-2}}{C''_{11}C''_{-2-2}}$$

$$\left.+\frac{a_{0-2}C'_{1-1}}{C''_{11}C''_{-1-1}}\frac{C''_{-1-2}}{C''_{-2-2}} - \frac{a_{20}}{C''_{11}}\frac{C''_{12}}{C''_{22}} + \frac{a_{-20}C'_{2-2}C''_{12}}{C''_{11}C''_{22}C''_{-2-2}}\right]$$

$$-\frac{5}{2}\left(\frac{M_1+M_2}{2M_2}\right)^{\frac{1}{2}}\left[\frac{a_{0-2}C''_{-1-2}}{C''_{-1-1}C''_{-2-2}}+\frac{a_{0-1}C''_{12}C''_{12}}{C''_{11}C''_{22}C''_{-1-1}}\right]. \quad \ldots \quad (13)$$

The various a_{ij} and C_{ij} are defined by Mason (1954, 1957). Equations (11) and (12) are much simplified by expanding in powers of M. Thus, we have

$$[\alpha'_T]_1 = \tfrac{1}{2}(6C_{12}^*-5)\left[1-\left(\frac{8}{5}A_{12}^*-1\right)M+\frac{15}{2\sqrt{2}Z'}\left(1-\frac{8A_{12}^*}{15}\right)M^{3/2}\right.$$

$$\left.-3\left\{1-\frac{8}{15}A_{12}^*\left(\frac{8}{5}A_{12}^*-1\right)\right\}M^2+\ldots\right], \quad \ldots \quad (14)$$

and

$$[\alpha'_T]_2 = [\alpha_T]_1\left\{1+\frac{7}{25}(6C_{12}^*-5)^2+\frac{2}{5}(6C_{12}^*-5)B_{13}\right\}$$

$$\left\{[\alpha_T]_1(8B_{15}+\frac{24}{5}A_{12}^*)+\frac{1}{84}(8E_{11}^*-7)^2(6C_{12}^*-5)\right.$$

$$\left.\left(\frac{8}{5}A_{12}^*-1\right)-\frac{(6C_{12}^*-5)^2}{5}B_{13}\left(4B_{15}+\frac{24}{5}A_{12}^*-1\right)\right\}M$$

$$+\frac{(6C_{12}^*-5)^2}{5\sqrt{2}Z'}\left\{\frac{7}{4}(6C_{12}^*-5)-7(6C_{12}^*-5)(1+B_{15})\right.$$

$$\left.-10B_{13}(1+B_{15})+2(5-2A_{12}^*)B_{13}\right\}M^{3/2}$$

$$-\left[[\alpha_T]_1\left\{3-\frac{448A_{12}^{*2}}{25}+\frac{192}{35}K_{12}^*-\frac{192}{5}A_{12}^*B_{15}\right.\right.$$

$$\left.-16B_{15}^2\right\}-\left\{\frac{1}{84}(8E_{11}^*-7)^2(6C_{12}^*-5)\right.$$

$$\left(3-\frac{64A_{12}^{*2}}{25}+\frac{8A_{12}^*}{5}\right)-\frac{B_{13}}{5}(6C_{12}^*-5)^2$$

$$\left.\left.\left(\frac{448}{25}A_{12}^{*2}-6-\frac{192}{35}K_{12}^*-\frac{24}{5}A_{12}^*+\frac{96}{5}A_{12}^*B_{15}-4B_{15}\right)\right\}\right]M^2+\ldots \quad \ldots (15)$$

where

$$B_{15}=\frac{2(7A_{12}^*-8H_{12}^*)}{7(6C_{12}^*-5)}.$$

In writing Eq. (15) it has been tacitly assumed that $[\alpha_T]_1=[\alpha'_T]_1$ in K'_2 for a Lorentzian gas mixture. This procedure is valid and consistent with the Kihara approximation scheme was brought to our notice by Prof. E. A. Mason, and we are extremely grateful to him for this suggestion. If $M_1>>M_2$ so that M can be neeglected, we get the following simple expressions for $[\alpha'_T]_1$, adn $[\alpha'_T]_2$ respectively :

$$[\alpha'_T]_1^a=(1/2)(6C_{12}^*-5), \quad \ldots (16)$$

and

$$[\alpha'_T]_2^a=[\alpha_T]_1^a\left[1+\frac{7}{25}(6C_{12}^*-5)^2+\frac{2}{5}(6C_{12}^*-5)-\frac{3}{10}(5-4B_{12}^*)\right]. \quad \ldots (17)$$

These expressions have been already derived by Mason (1957) for a Lorentzian gas mixture.

DISCUSSION

The formulae derived in the previous section will be extremely useful for calculating the thermal diffusion factor of binary mixtures when the lighter component is in trace or is a radioactive tracer. The experiments of the latter type are not yet performed though data on such systems will be interesting to determine. Before putting any confidence in the various formulae it will be essential to estimate their adequacy. In this section we will report the results of numerical calculations for a few mixtures to throw light on this point. Numerical computations of this nature for ideal Lorentzian gas mixtures were performed by Mason (1957). The values of thermal diffusion factor obtained by considering terms having powers of M as zero, one, one and a half, and two will be referred to as $[\alpha'_T]^a$, $[\alpha'_T]^b$, $[\alpha'_T]^{b'}$ and $[\alpha'_T]^c$ respectively

TABLE I

Various calculated values of α'_T as a function of temperature for *Ar-Xe* and *He-Xe* mixtures with the lighter component present only in trace

System	T °K	$[\alpha'_T]_1$	$[\alpha'_T]_2$	$[\alpha'_T]^a{}_2$	$[\alpha'_T]^b{}_2$	$[\alpha'_T]^{b'}{}_2$	$[\alpha'_T]^c{}_2$
	100	−0 0248	−0 0250	−0 0245	−0 0251	−0 0251	−0 0247
	200	0.0326	0 0305	0 0282	0.0312	0.0318	0.0296
	300	0 0969	0 0880	0 0855	0 0870	0 0867	0.0866
	400	0 143	0.133	0.133	0.132	0.129	0 131
	500	0.171	0 163	0 170	0.160	0.155	0 160
	700	0 209	0 199	0 214	0.193	0 183	0.199
	900	0.229	0.223	0.242	0 212	0.200	0.222
He-Xe	200	0 270	0.255	0 257	0.254	0.254	0.255
	300	0.307	0.301	0.307	0 303	0.303	0.303
	500	0 329	0.340	0.346	0.341	0.341	0.341
	700	0.332	0.340	0.353	0.348	0.347	0.350
	900	0 335	0.350	0.355	0.349	0.348	0.349

The calculated values of the thermal diffusion factor as a function of temperature for the Ar-Xe system, Ar, present only in trace, and He-Xe system with He in trace, are recorded in Tables I and II. These calculations are according to the familiar Lennard- Jones (12-6) intermolecular potential in conjunction with the

potential parameters of Lunbeck (1951). It is seen from Table I that for the Ar-Xe system where the value of M is appreciable, consideration of terms upto M^2 is sufficient. For systems where M is small $[\alpha'_T]_2^b$ may be even sufficient. Thus, for the He-Xe system we find that the contribution of terms having powers of M greater than one is negligible, so that $[\alpha'_T]_2 = [\alpha'_T]_2^b$. It is important to notice in Table I that the convergence of α'_T is poor though the degree depends on the specific system and temperature range, and will have to be investigated in each case individually. Simpler formulae worked out in this paper are specially suited for this work. In any case it seems very likely that the convergence error in most of the cases will be greater than the precision of the experimental measurements. Some caution is, therefore, needed for interpreting experimental data on this end of the composition range.

TABLE II

Calculated values of α_T as a function of temperature for *Ar-Xe* and *He-Xe* systems when the lighter component is present in trace

System	T °K	$[\alpha_T]_1$	$[\alpha_T]_2$	$[\alpha_T]_2^{approx*}$
Ar-Xe	100	−0 0250	−0 0234	−0.0181
	300	0 0896	0.0887	0 0977
	500	0 159	0 167	0 200
	700	0.189	0 202	0.238
	900	0.206	0.212	0.248
He-Xe	300	0.260	0 280	0.279
	500	0.284	0.309	0.304
	700	0 288	0.295	0.306
	900	0.285	0.318	0 313

*Values obtained according to Eqs. (9) and (10).

Similarly, computed values of α_T for these two systems and as a function of temperature are reported in Table II. Some conclusions are straightforward. The convergence of α_T is quite poor in this case too and is worse than on Kihara approximation scheme for these two systems. Unlike Kihara approximation results; the simpler and approximate formula derived on Chapman-Cowling scheme has poor validity for the Ar-Xe mixtures; however, it is somewhat adequate for the He-Xe system.

CONCLUSION

The convergence of the theoretical expressions for α_T is poor for approximately Lorentzian gas mixtures i.e. $X_1 \simeq X_2$ but $M_1 \simeq M_2$ is not necessarily true. The degree differs from mixture to mixture and the temperature range and will have to be investigated individually. Simpler formulae derived in this paper will facilitate such an investigation and will considerably reduce the computational labour. It would be very interesting to develop a third approximation scheme which may have better convergence error than either of the two discussed in this paper.

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